THERMOPHYSICAL PROPERTIES OF SODIUM β″-ALUMINA POLYCRYSTALLINE CERAMIC

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Abstract—The thermal diffusivity, heat capacity and thermal conductivity of solid samples of new, Li-stabilized, sodium β″-alumina polycrystalline ceramic have been determined in the temperature range 500–1200 K. Unit cell parameters and the coefficient of thermal expansion have been determined using X-ray diffraction in the range 300–1273 K for similar solid ceramic samples which had been exposed to liquid sodium at high temperature as well as for new samples. Some differences in unit cell parameters were found between sodium exposed and unexposed samples.

INTRODUCTION

Sodium β″-alumina polycrystalline ceramic is a solid electrolyte which is used in high-temperature devices such as the sodium-sulfur battery, which operates at 595–625 K, and the Alkali Metal Thermal to Electric Converter (AMTEC), which operates at 900–1200 K. Understanding of the operating characteristics of these devices requires that physical properties of β″-alumina be known over the temperature range 300–1200 K. The thermal diffusivity, heat capacity and thermal conductivity of β″-alumina were determined in the range 500–1200 K, and high-temperature X-ray diffraction studies were made in the range 300–1273 K. Unit cell parameters as functions of temperature were used to determine the coefficient of thermal expansion of this material. Both sets of measurements were done on small pieces of commercially available Li-stabilized Na-β″-alumina with nominal composition $Na_{1.67}Li_{0.33}Al_{10.67}O_{17}$. The X-ray diffraction studies were done on two sets of samples: those that had been immersed in liquid sodium at high temperature ("doped") and those that had not ("undoped"). The thermal studies were made only on samples which had not been exposed to liquid sodium.

EXPERIMENTAL

Thermophysical characteristics of β″-alumina

The thermal diffusivity and heat capacity of ceramic β″-alumina solid electrolyte (BASE) were measured directly on disk-shaped samples 12–15 mm in diameter and 1–1.5 mm thick, using a flash method [1] with corrections for heat loss and pulse time effects [2]. In this method, a rapid "flash" of radiant energy is deposited on one face of a disk-shaped sample and the temperature of the other face monitored as a function of time. Analysis of these data allows determination of thermal diffusivity and heat capacity. Thermal conductivity may be calculated from the thermal diffusivity, Δ, heat capacity, C_p, and density, ρ, where thermal conductivity, $k = \Delta C_p \rho$.

Two samples were used for measurements to determine thermal diffusivity, heat capacity and thermal conductivity. Sample 1 was heated in air to 1273 K for 2 h, and stored under argon until it was tested. Sample 2 was heated under a bed of β″-alumina powder in air at 1573 K for 3 h. Heat capacity, and thus thermal conductivity data from sample 1 were not reproducible above 900 K, and so are not included here.

X-Ray diffraction studies

High temperature X-ray diffraction (HTXRD) data were collected on a Scintag XDS-2000 Theta: Theta diffractometer equipped with an Edmund Buehler Model HKD 2.4 high temperature furnace, a copper X-ray tube, and a liquid nitrogen cooled, intrinsic germanium solid state detector. Temperature measurements were made using a W/WRe thermocouple welded to the underside of the furnace's heating strip. A radiant surrounding heater was also
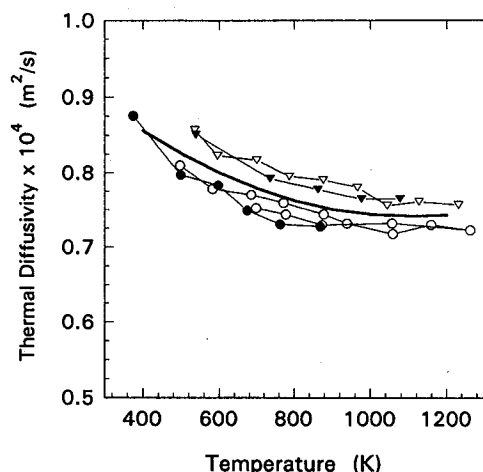
Fig. 1. The thermal diffusivity of β ''-alumina polycrystalline ceramic was measuring using a flash method. Circles are sample 1, triangles are sample 2. The heavy line is the smoothed value of thermal diffusivity.

used to minimize temperature gradients between the heating strip and the top surface of the sample.

Several $10 \times 10 \times 1$ mm samples of polycrystalline β ''-alumina ceramic were studied in these experiments. The β ''-alumina was obtained from Ceramatec, Inc. Two types of samples were studied, β ''-alumina ceramic which had been exposed to sodium by immersion in liquid sodium for 6 h at 1073 K ("doped" samples) and samples which had not been exposed to sodium and had been annealed in air at 1273 K for 1 h ("undoped" samples). Doped samples appeared black after immersion in liquid sodium. Samples were affixed to the furnace heating strip with small amounts of vaseline. The chamber

was sealed and evacuated to a pressure $< 10^{-5}$ torr. Height variations in the samples were compensated by adjusting the furnace height relative to the center of the diffractometer, until peak positions for the β ''-alumina (003) and (006) peaks agreed.

All HTXRD measurements were made under computer control. Digital diffraction data on the undoped samples and on one of the doped samples were obtained with continuous scans from $2\theta = 2°$ to $2\theta = 60°$ at rates of $1°$ min^{-1} or $2°$ min^{-1} at intervals of $0.02°$. The heating rate for these samples was 10 K min^{-1}. Temperature was held at each measurement temperature for 10 min to establish thermal equilibrium before diffraction scans were started. Diffraction data on another doped sample were obtained with continuous scans from $2\theta = 2°$ to $2\theta = 72°$ at a rate of $0.5°$ min^{-1} at intervals of $0.02°$. The heating rate for this sample was 50 K min^{-1} with the temperature held for 10 min before scans were begun.

Incorporation of an internal standard was not possible in these samples; consequently, refinements of the unit cell parameters were done using the least-squares unit-cell refinement computer program CELLSVD, which can include explicitly the refinement of systematic errors or geometric aberrations during a unit cell refinement [3].

RESULTS

Thermophysical properties of BASE were determined in the temperature range 535–1230 K. The thermal diffusivity of the two samples is shown in Fig. 1. Successive measurements of diffusivity on each
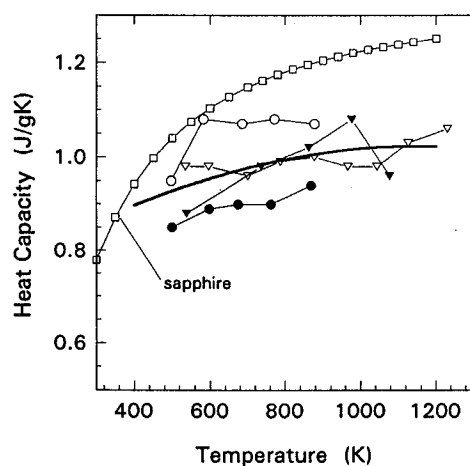
(a)
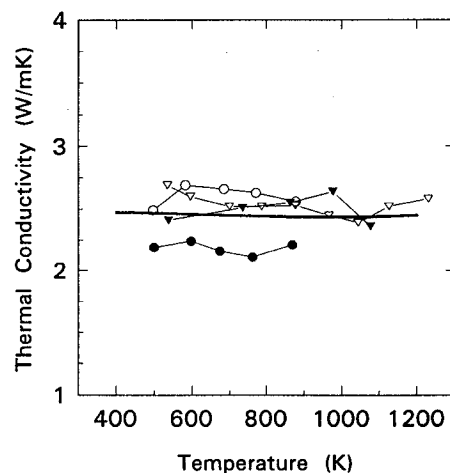
(b)

Fig. 2. Heat capacity (a) and thermal conductivity (b) of sodium β ''-alumina were determined for the same samples of β ''-alumina used in Fig. 1. The results of both samples were used to determine a smooth curve (heavy lines).

Table 1. The lattice parameters for sodium β''-alumina samples, measured as a function of temperature and refined using the CELLSVD program. The estimated standard deviation in the last two digits for each value is noted in parentheses

Temperature (K)	a undoped	c undoped	a doped	c doped
UP				
300	5.6064 (04)	33.437 (02)	5.6107 (06)	33.473 (04)
473	5.6151 (05)	33.482 (03)	5.6143 (09)	33.482 (05)
673	5.6206 (04)	33.511 (02)	5.6158 (17)	33.497 (12)
823			5.6184 (03)	33.518 (02)
873	5.6182 (04)	33.501 (02)		
1073	5.6277 (04)	33.552 (02)	5.6277 (15)	33.566 (09)
1273	5.6398 (05)	33.620 (03)	5.6362 (06)	33.603 (03)
DOWN				
1073	5.6270 (04)	33.545 (02)	5.6220 (06)	33.536 (04)
873	5.6222 (05)	33.527 (03)		
823			5.6194 (05)	33.516 (04)
673	5.6159 (05)	33.489 (03)	5.6129 (07)	33.488 (04)
473	5.6113 (04)	33.472 (02)	5.6113 (12)	33.462 (05)
300	5.6068 (07)	33.440 (04)	5.6060 (12)	33.440 (05)

sample were reproducible within 2% for each sample, although the diffusivity for sample 2 was some 5–8% larger than that of sample 1. The difference between samples 1 and 2 is somewhat larger than typical accuracy of the measurement, and may therefore represent a small but real difference between the samples. The smoothed value for the diffusivity is also shown in Fig. 1. Thermal diffusivity, Δ, is given to $\pm 4\%$ by:

$$\Delta = 1.024 \times 10^{-6} - 5.122 \times 10^{-10}T$$
$$+ 2.312 \times 10^{-13}T^2 \, \text{m}^2 \, \text{s}^{-1},$$

where T is the temperature in K.

The heat capacity and thermal conductivity of BASE are shown in Fig. 2(a) and (b). These data show the thermal conductivity to be fairly flat over the temperature range and to have a value $\sim 2.45 \, \text{W m}^{-1} \, \text{K}^{-1}$. The heat capacity shown in Fig. 2(a) is somewhat lower than the heat capacity of sapphire, also in the figure. The smoothed value of the heat capacity is shown by the heavy curve in Fig. 2(a) and is given to $\pm 9\%$ by the expression:

$$C_p = 0.7321 + 5.006 \times 10^{-4}T$$
$$- 2.151 \times 10^{-7}T^2 \, \text{J gK}^{-1},$$

where T is the temperature in K.

The thermal conductivity is calculated as the product $\Delta C_p \rho$. A density, ρ, of $3.22 \, \text{g cm}^{-3}$ was determined from the mass and dimensions for each
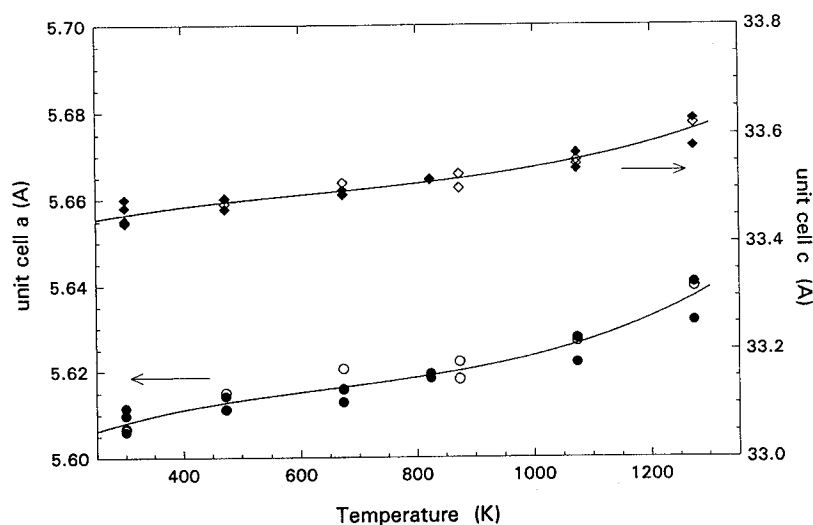

Fig. 3. The unit cell parameters a and c were determined at nominal temperatures 300–1273 K for sodium exposed ("doped") and unexposed ("undoped") samples of sodium β''-alumina ceramic. Open symbols are data for undoped, filled symbols are data for doped samples. The lines are third order polynomial fits of the combined data.
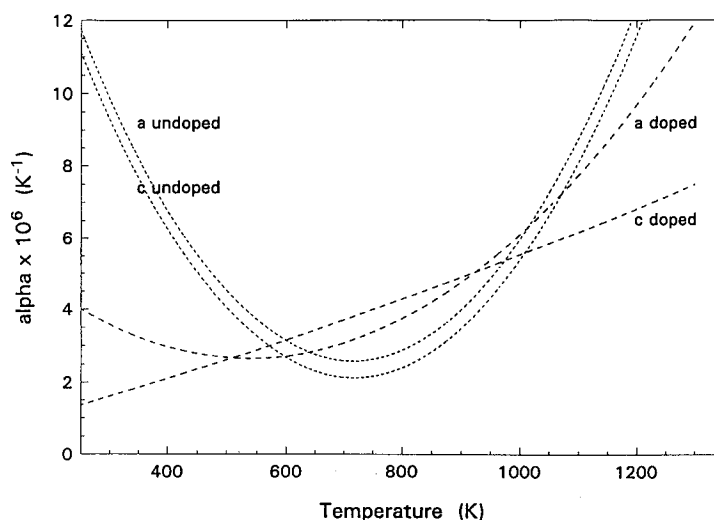
Fig. 4. The temperature dependence of the coefficient of thermal expansion α_T of doped and undoped sodium β''-alumina was determined from the fits to the unit cell parameters shown in Fig. 3.

sample. Thermal conductivity, k, shown in Fig. 2(b), is given to $\pm 20\%$ and -13% by $k = 2.451 + 2.456 \times 10^{-4} T - 6.178 \times 10^{-7} T^2 + 4.275 \times 10^{-10} T^3 - 6.993 \times 10^{-14} T^4 \, \text{W} \, \text{m}^{-1} \text{K}$ where T is the temperature in K.

Refined unit cell parameters calculated from temperature dependent X-ray diffraction data are given in Table 1. Temperatures in the tables as well as in the figures are nominal temperatures, measured at the heating strip. As shown in Fig. 3, differences between the unit cell parameters of doped and undoped samples exist, but are not large. After completing a cycle of data collection on doped samples, they no longer appeared black, but grey. Any loss of sodium which had been incorporated in the ceramic during

doping probably occurred at temperatures > 1000 K; there was no apparent effect of sodium loss on lattice parameters at temperatures < 1073 K. Coefficients of thermal expansion were calculated separately for doped and undoped samples, as shown in Fig. 4, and from the combined data, as shown in Fig. 5.

The coefficients of thermal expansion, α, shown in Figs 4 and 5, were calculated by fitting a plot of the lattice parameters vs temperature to a third order polynomial, taking the temperature derivative of the polynomial, and inserting the result into the expression:

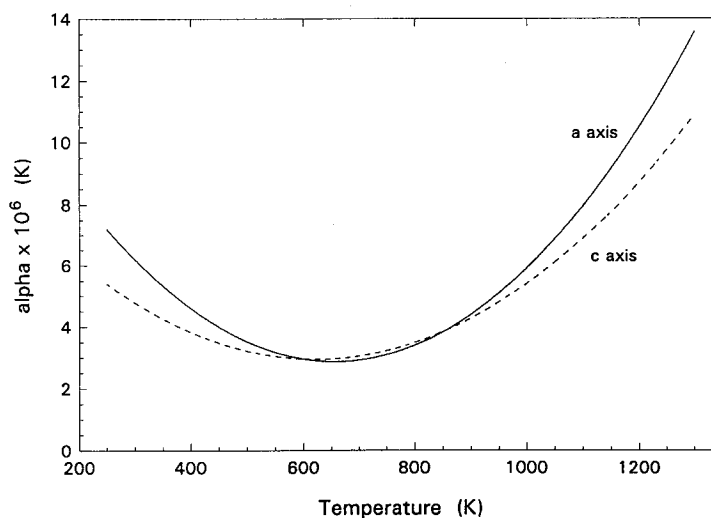$$\alpha_T = \frac{1}{a_T} \frac{da}{dT},$$

Fig. 5. The temperature dependence of the coefficient of thermal expansion was determined from the combined doped and undoped β''-alumina ceramic unit cell parameters.

Table 2. Thermal expansion coefficients for Li_2O stabilized Na-β''-alumina ceramic pieces, calculated from X-ray data taken in vacuum

Temperature range (K)	α undoped ($\times 10^{-6} K^{-1}$)		α doped ($\times 10^{-6} K^{-1}$)		α all ($\times 10^{-6} K^{-1}$)		α avg. ($\times 10^{-6} K^{-1}$)	Reference
	a	c	a	c	a	c		
300–1273	6.09	5.56	4.03	3.47	5.16	4.65	4.91	this work
673–1273	6.41	5.98	5.18	4.26	5.80	5.12	5.46	this work
573–1273[a]	7.8	5.0						[8]
300–675[b]							7.2	[6]
298–773[c]							6.8	[8]
673–1273[d]	7.8	7.3						[9]

[a]Powders, X-ray data taken in He.
[b]Dilatometry, stabilizer and atmosphere not stated.
[c]Dilatometry, ceramic bars, taken in Ar (combined α).
[d]MgO stabilized Na-β''-alumina powders, X-ray data taken in air.

where α_T is the coefficient of thermal expansion at a given temperature and a_T is the lattice parameter at the same temperature [4]. The expressions which describe α_T as a function of temperature (K) for doped and undoped samples, and for α_T for the combined data are:

a, undoped:
$$\alpha_T = 2.399 \times 10^{-5} - 5.969 \times 10^{-8}T + 4.166 \times 10^{-11} T^2$$

c, undoped:
$$\alpha_T = 2.315 \times 10^{-5} - 5.846 \times 10^{-8}T + 4.071 \times 10^{-11} T^2$$

a, doped:
$$\alpha_T = 7.285 \times 10^{-6} - 1.712 \times 10^{-8}T + 1.594 \times 10^{-11} T^2$$

c, doped:
$$\alpha_T = 2.059 \times 10^{-7} + 4.424 \times 10^{-9}T - 9.114 \times 10^{-13} T^2$$

a, comb:
$$\alpha_T = 1.410 \times 10^{-5} - 3.413 \times 10^{-8}T + 2.595 \times 10^{-11} T^2$$

c, comb:
$$\alpha_T = 9.730 \times 10^{-6} - 2.173 \times 10^{-8}T + 1.741 \times 10^{-11} T^2.$$

For comparison to previously reported values, the coefficient of linear thermal expansion has been calculated over a temperature range ΔT according to:

$$\alpha = \frac{1}{a_0} \frac{\Delta a}{\Delta T},$$

where a_0 is the lattice parameter at 300 K. These values are tabulated in Table 2.

DISCUSSION

The measured heat capacity at 1200 K is 1.02 J g^{-1} K^{-1}, compared to the Debye value for the heat capacity of 1.23 J g^{-1} K^{-1} calculated from the nominal composition. For comparison, Fig. 2(a) also shows the heat capacity of sapphire, which was reported to have an error of 0.2% [5]. The accuracy of the heat capacity determined using the flash method relies on the nature of the surface of the sample. In the calculations, each sample is assumed to absorb the flash of radiation in the same way as the materials used for calibration; the sample surfaces are therefore treated in order to provide absorption characteristics which are as standard and as reproducible as possible. Tantalum was sputtered onto each sample to act as a diffusion barrier; graphite was then sputtered onto each sample. It is possible for the surface characteristics to vary with exposure to air or high temperatures. In addition, any differences in adherence of the sputtered materials, surface texture or reaction may affect the results of the heat capacity measurement. In any case, the thermal diffusivity measurement, shown in Fig. 1, depends only on sample thickness and time, and thus is an accurate measurement.

Typically, as in the case of sapphire, the heat capacities of solids are relatively close to or greater than (by 10–20%) the Debye value at high temperatures. Rarely are high temperature heat capacities significantly less than the Debye value. Based on either calculated values or experimental values for sapphire, the measured heat capacity of β''-alumina appears to be up to 20% less than expected. The actual heat capacity and thermal conductivity, therefore, may be as much as 20% larger than shown in Fig. 2. The thermal conductivity is nearly temperature independent between 500 and 1200 K, with a value ~ 2.45 W m^{-1} K^{-1} and an estimated error of $+20\%$ and -13%. Temperature independent thermal conductivity is typically observed in highly disordered materials such as glasses and crystalline materials with random occupancy of atomic sites.

Thermal diffusivity, heat capacity and thermal conductivity of polycrystalline β''-alumina have been previously measured at 680 K and published [6]. The values reported in this work are in good agreement with the previously reported values.

The thermal expansion coefficients calculated for these polycrystalline samples are somewhat lower than those previously reported; values from this work and earlier values are tabulated in Table 1. In earlier studies, X-ray data were taken on ground (powder) samples of ceramic, in contrast to this study where data were taken on ceramic pieces. Solid polycrystalline samples were used in order to obtain thermal expansion data which may be applied directly to ceramics used in devices operating at high temperatures. Because of the constraint to expansion of the unit cell provided by the solid sample, unit cells cannot expand anisotropically, and the measured expansion may be less than that measured in a powder sample.

In some temperature ranges, expansion in doped samples is less than expansion in undoped samples. When the ceramic samples are immersed in liquid sodium, sodium atoms are incorporated into the ceramic, probably at grain boundaries, and microdroplets may form at voids in the ceramic [7]. Sodium atoms do not move easily either in or out of the ceramic at temperatures below ~ 750 K, and require heating for a few hours in vacuum at $T > 1000$ K to remove them [10]. In spite of the observed change in color after heating of the doped samples, any loss of sodium which was incorporated into the sample does not appear to affect the lattice parameters, as may be seen in Table 1.

Heating doped samples in vacuum (10^{-5} torr) at 1273 K may lead to some Na_2O formation, and subsequent incorporation of Na_2O in the crystallites. Undoped samples may tend to lose strongly bound H_2O from the lattice, or CO_2 from Na_2CO_3 at the grain boundaries. When the doped samples are cooled, any Na_2O which may have entered the crystal structure remains incorporated and the lattice correspondingly expanded. This incorporation accounts for the unit cell parameters of doped β''-alumina, especially c, being larger than those of undoped samples. In addition, as the doped sample unit cells may be already expanded, undoped samples have a greater possibility of expansion upon heating, and thus may have a larger coefficient of expansion on heating than do doped samples.

Values for the coefficient of thermal expansion of β''-alumina determined from combined doped and undoped data have been included in this study. There is evidence that the mechanical characteristics of β''-alumina under operation in sodium vapor atmosphere are intermediate between unexposed (undoped) and sodium exposed (doped) ceramic [7]. In addition, ceramic which has been operated in an AMTEC cell at $T > 1000$ K appears grey or black on the high pressure side of the electrolyte, indicating some sodium incorporation into the ceramic. Accordingly, thermal expansion of ceramic under operating conditions may be expected to be intermediate between that of doped and undoped β''-alumina.

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